

PCT

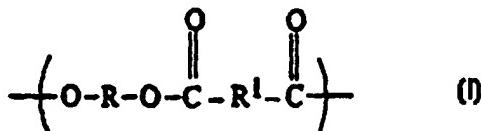
WORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau



INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁶ : C08L 67/02, 69/00 // (C08L 67/02, 69:00)	A1	(11) International Publication Number: WO 99/63002 (43) International Publication Date: 9 December 1999 (09.12.99)
(21) International Application Number: PCT/US99/10864		(81) Designated States: JP, European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).
(22) International Filing Date: 17 May 1999 (17.05.99)		Published <i>With international search report.</i>
(30) Priority Data: 09/087,777 29 May 1998 (29.05.98) US 09/277,760 29 March 1999 (29.03.99) US		
(71) Applicant: GENERAL ELECTRIC COMPANY [US/US]; 1 River Road, Schenectady, NY 12345 (US).		
(72) Inventor: HOEFFLIN, Frank; 1512 Irvington Avenue, Evansville, IN 47712 (US).		
(74) Agents: WINTER, Catherine, J. et al.; General Electric Company, 3135 Easton Turnpike W3C, Fairfield, CT 06431 (US).		

(54) Title: POLYCARBONATE POLYESTER RESIN MOLDING COMPOSITION WITH GOOD IMPACT PROPERTIES



(57) Abstract

A thermoplastic resin comprising a miscible resin blend of a ductile resin containing greater than about 60 percent by weight repeating units of an aryl polycarbonate, and a polyester resin wherein ratio of polyester resin to ductile resin is from about 60 to 40 to about 85 to about 15, wherein the polyester consist essentially of a polyester having formula (I) where R and R¹ are cycloalkyl or cycloalkyl containing radicals. Preferred are blends of an aromatic polycarbonate or a polyestercarbonate and a cycloaliphatic polyester like poly(1,4-cyclohexanedimethylene-1,4-cyclohexane dicarboxylate) stabilized with acidic phosphorus compounds.

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AL	Albania	ES	Spain	LS	Lesotho	SI	Slovenia
AM	Armenia	FI	Finland	LT	Lithuania	SK	Slovakia
AT	Austria	FR	France	LU	Luxembourg	SN	Senegal
AU	Australia	GA	Gabon	LV	Latvia	SZ	Swaziland
AZ	Azerbaijan	GB	United Kingdom	MC	Monaco	TD	Chad
BA	Bosnia and Herzegovina	GE	Georgia	MD	Republic of Moldova	TG	Togo
BB	Barbados	GH	Ghana	MG	Madagascar	TJ	Tajikistan
BE	Belgium	GN	Guinea	MK	The former Yugoslav Republic of Macedonia	TM	Turkmenistan
BF	Burkina Faso	GR	Greece	ML	Mali	TR	Turkey
BG	Bulgaria	HU	Hungary	MN	Mongolia	TT	Trinidad and Tobago
BJ	Benin	IE	Ireland	MR	Mauritania	UA	Ukraine
BR	Brazil	IL	Israel	MW	Malawi	UG	Uganda
BY	Belarus	IS	Iceland	MX	Mexico	US	United States of America
CA	Canada	IT	Italy	NE	Niger	UZ	Uzbekistan
CF	Central African Republic	JP	Japan	NL	Netherlands	VN	Viet Nam
CG	Congo	KE	Kenya	NO	Norway	YU	Yugoslavia
CH	Switzerland	KG	Kyrgyzstan	NZ	New Zealand	ZW	Zimbabwe
CI	Côte d'Ivoire	KP	Democratic People's Republic of Korea	PL	Poland		
CM	Cameroon	KR	Republic of Korea	PT	Portugal		
CN	China	KZ	Kazakhstan	RO	Romania		
CU	Cuba	LC	Saint Lucia	RU	Russian Federation		
CZ	Czech Republic	LI	Liechtenstein	SD	Sudan		
DE	Germany	LK	Sri Lanka	SE	Sweden		
DK	Denmark	LR	Liberia	SG	Singapore		
EE	Estonia						

POLYCARBONATE POLYESTER RESIN MOLDING COMPOSITION
WITH GOOD IMPACT PROPERTIES

BACKGROUND OF THE INVENTION

FIELD OF THE INVENTION

- 5 The invention relates to blends of a polycarbonate resin with a polyester resin.

BACKGROUND OF THE INVENTION

Aromatic polycarbonates (PC) are well known and exhibit properties of extreme toughness, transparency, resistance to burning and 10 in general, maintenance of useful properties over a wide temperature range. However, polycarbonate has an increased Y.I. yellowness index, after exposure to light. Hence, it is desirable to enhance the weatherability of polycarbonate. Although polycarbonates exhibit high impact strength, it is desirable to obtain even higher impact strength. When considering 15 mixtures, blends and additives to polycarbonate, it is difficult to obtain an improvement of one property without deleteriously affecting other desirable properties.

U.S. Patent 4,391,954 to Scott describes an aromatic carbonate polymer having improved hydrolysis resistance. The polycarbonate 20 includes a polyester polymer derived from cyclohexanedimethanol. As set forth, column 3, lines 4 to 7, "The preferred polyester resins may be derived from the reaction of either the cis- or trans- isomer (or a mixture thereof) of 1,4-cyclohexanedimethanol with a mixture of iso- and terephthalic acids."

U.S. Patent 5,486,562 describes UV-stable weatherable molding compositions based upon cycloaliphatic diacid derived polyester materials containing impact-modifying elastomeric polymers and filler such as glass fibers, which compositions have enhanced melt flow properties while 5 retaining good impact strength properties. The modulus of these compositions is low and while stiffness can be improved with added filler, like fiberglass, impact strength is reduced.

U.S. Patent 5,410,000 discloses molding compositions containing poly(cycloalkyl/aryl) polyesters and mixtures thereof with other 10 polymeric binder materials including polycarbonates, together with impact modifying polymers and reinforcing fillers.

U.S. Patent 5,399,661 discloses molding compositions containing poly(cycloalkyl/aryl) polyesters and mixtures thereof with other polymers, core shell impact modifiers and fillers. These aromatic 15 cycloalkyl esters do not have good weatherability.

U.S. Patent 5,260,379 discloses thermoplastic molding compositions comprising blends of aromatic polyester resins and styrene copolymers containing up to about 35 mol% methyl methacrylate and having good ductility and melt flow properties. Glass fiber reinforcing filler may be 20 included as well as "impact modifiers". Specific blends containing 25, 50 and 75 weight percent of each of these styrene copolymers are disclosed but no specific impact modifier is disclosed as an additive to such blends.

U.S. Patent 3,657,389 discloses hot melt adhesive compositions based upon polymer blends of cycloaliphatic polyesters and olefin 25 polymers including acrylate and methyl methacrylate co-polymers. Fillers may be included but impact modifiers are not disclosed.

U.S. Patent 5,115,016 discloses aromatic polyester resin molding compositions comprising a crystalline polyethylene terephthalate, reinforcing glass fiber and a thermoplastic poly(methyl methacrylate) modifier resin which improves the gloss and reduces warp of articles 5 molded therefrom.

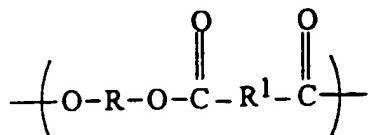
The present invention relates to molding compositions based upon blends of thermoplastic polycarbonate resin and a thermoplastic polyester resin which have outstanding impact resistance, good processability, and transparency. The impact is greater than would be expected from a just a 10 mixture of the components.

SUMMARY OF THE INVENTION

The polycarbonate polyester molding compositions of the present invention comprise a polycarbonate resin component and a cycloaliphatic polyester component. The ductile polycarbonate component is an aryl 15 polycarbonate, a polyester carbonate or a "soft segment" aliphatic-polyester carbonate. The cycloaliphatic component is substantially devoid of aromatic constituents.

In accordance with the present invention there is provided a miscible resin blend comprising a ductile polycarbonate, aromatic 20 polyester carbonate or aliphatic polyester carbonate and a cycloaliphatic polyester resin wherein ratio of polyester to ductile resin is from about 50 to 50 to about 95 to about 5.

The polyester resin comprises a polyester having repeating units of the formula I:



where R and R¹ are cycloalkyl or cycloalkyl containing radicals.

The polyester is a condensation product where R is the residue of a cycloalkane containing diol having 6 to 20 carbon atoms or chemical equivalent thereof, and R¹ is the decarboxylated residue derived from a cycloalkane containing diacid of 6 to 20 carbon atoms or chemical equivalent thereof.

The resulting blend has a Notched Izod (NI) as determined by ASTM D256 test procedure greater than either the Notched Izod of the 10 individual polycarbonate component or polyester component of the blend.

In one case, a miscible polycarbonate/polyester blend of the present invention exhibits a surprisingly low notch sensitivity with Notched Izod values as high as 25 ft. lbs./in. at 23°C and surpass the ductility of neat polycarbonate by up to 65 percent. More surprisingly, 15 this effect is achieved without the use of an impact modifier so that the resulting blends are transparent.

This specific combination of polycarbonate resins with cyclic alkyl polyesters solves problems of UV degradation while enhancing impact strength. The resulting product has improved flow and toughness as 20 compared to polycarbonate, higher heat resistance than cycloaliphatic polyester, and retains transparency with surprising ductility.

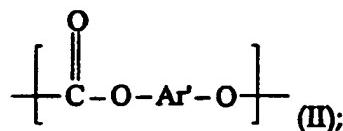
It is also important to prevent reaction between the polycarbonate and the polyester during melt processing, since such reaction will lead to

copolymer formation and a degradation of thermal properties, as well as the creation of color and undesirable processing effects such as gas generation. Use of specific acidic phosphorus species is desirable to prevent melt reaction of the blended polymers. Additional ingredients 5 may include rubbery modifiers such as core shell, graft or linear, random and block copolymers.

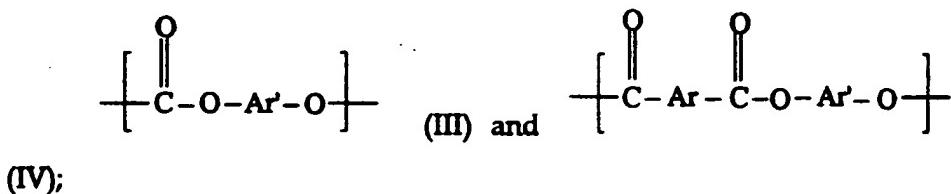
Detailed Description

The ductile resin which is a resin selected from the group consisting of

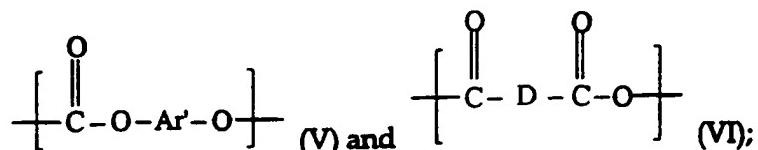
- 10 a) a polycarbonate resin made up of recurring aryl polycarbonate units of the formula II;



- 15 b) an aromatic polyester carbonate made up of recurring polycarbonate units of formula III and recurring polyester units of the formula IV;



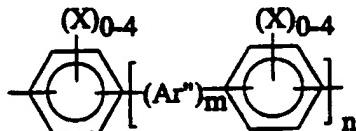
- 20 c) an aliphatic polyester carbonate made up of recurring polycarbonate units of the formula V and recurring carboxylic chain units of the formula VI;



or d) mixtures of a) or b) or c).

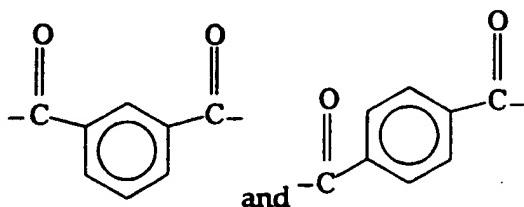
Ar' is a divalent aromatic radical residue of the dihydric phenol employed in the preparative polymerization reaction of the polycarbonate.

- 5 Preferred divalent residue of dihydric phenols, Ar' are represented by the general formula:



- wherein Ar'' is a divalent hydrocarbon radical containing from 1 to about 15 carbon atoms or a substituted divalent hydrocarbon radical containing from 1 to about 15 carbon atoms; each X is independently selected from the group consisting of hydrogen, halogen, and a monovalent hydrocarbon radical such as an alkyl group of from 1 to about 8 carbon atoms, an aryl group of from 6 to about 18 carbon atoms, an aralkyl group of from 7 to about 14 carbon atoms, an alkoxy group of from 1 to about 8 carbon atoms; and m is 0 or 1 and n is an integer of from 0 to about 5. Ar'' may be a single aromatic ring like hydroquinone or resorcinol, or a multiple aromatic ring like biphenol or bisphenol A. the more preferred dihydric phenol employed comprises greater than 70 percent by weight bisphenol A with the remaining portion comprising 20 dihydric phenol residue of the above formula.

- Ar is a divalent aliphatic, alicyclic or aromatic radical, or mixtures thereof of the condensation product from a dicarboxylic acid or derivative thereof. Preferably Ar is a C₆-C₂₀ aryl radical comprising a decarboxylated residue derived from an aromatic dicarboxylic acid. Ar is
- 5 most preferably the residue from iso- and terephthalate or mixtures thereof having the formula:



- D is an diivalent aliphatic radical of the condensation product from an aliphatic diol. Preferably D is a divalent alkylene radical containing 2 to
- 10 18 carbon atoms, more preferably A has the formula -(CH₂)_n wherein n is an integer of from 2 to 18, more preferably from 2 to 6.

- D is the divalent aliphatic residue from the dicarboxylic acid which results when a dihydric phenol is phosgenated in the presence of the dicarboxylic acid or derivative thereof. Preferably D is an divalent alkyl
- 15 radical of from C₂ to C₃₆, more preferably from C₆ to C₁₆, with the preferred formula -(CH₂)_n.

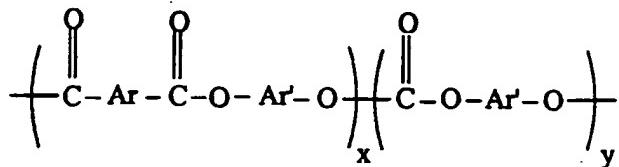
- The preferred component a) is an aromatic carbonate homopolymer, e.g., a homopolymer derived from 2,2-bis(4-hydroxyphenyl)propane (bisphenol-A) and phosgene, commercially
- 20 available under the trade designation LEXAN Registered TM from General Electric Company.

The preferred polycarbonates are preferably high molecular weight aromatic carbonate polymers have an intrinsic viscosity (as measured in methylene chloride at 25°C.) ranging from about 0.30 to about 1.00 dl/gm. Polycarbonates may be branched or unbranched and generally will have a 5 weight average molecular weight of from about 10,000 to about 200,000, preferably from about 20,000 to about 100,000 as measured by gel permeation chromatography. It is contemplated that the polycarbonate may have various known end groups.

According to the present invention, the impact resistance of a high 10 impact weatherable polycarbonate/polyester molding composition can be substantially improved by blending the previously mentioned polyester containing cycloalkyl radials to form a molding composition having a substantially greater toughness than could be predicted according to the rule of mixtures.

15 The present cycloaliphatic polyesters are condensation products of aliphatic diacids, or chemical equivalents, and aliphatic diols, or chemical equivalents. The present cycloaliphatic polyesters may be formed from mixtures of aliphatic diacids and aliphatic diols but must contain at least 80 mole % of cyclic diacid and/or cyclic diol components, the remainder, if 20 any, being linear aliphatic diacids and/or diols. The cyclic components are necessary to impart good rigidity, and they do not absorb UV under normal exposure conditions, thereby providing rigid molded articles having excellent weatherability properties. Aromatic components are not preferred since, to the extent they are present, they impart enhanced UV- 25 absorbance leading to degraded weatherability properties.

The preferred component b) is a polyester carbonate which may be represented by the following formula:



In the preferred ductile resin containing repeating polycarbonate units as set forth in formula II, x and y represent the respective weights of ester units and polycarbonate units based on 100 parts total weight. When x is 0, the polyester linkages are absent and the resin is known as a polycarbonate resin. When y is greater than about 5 percent by weight, the resin is known as a polyester carbonate resin (PEC resin). In a preferred resin of the present invention, x is from about 60 to about 95 mole percent. Poly(ester-carbonate) resins, also commonly referred to as copolyester-polycarbonate resins, are copolymers of aromatic diphenols reacted with dicarboxylic acids and carbonic acid or their derivatives.

Melt polymerization methods to make PEC resins may involve co-reacting, for example, various mixtures of dihydric phenols and ester precursors such as, for example, diphenyl derivatives of iso- and terephthalates, and their mixtures. Diphenyl carbonate may be introduced to prepare polyester carbonate copolymers. Various catalysts or mixtures of catalysts such as, for example, lithium hydroxide and lithium stearate can also be used to accelerate the polymerization reactions.

In general, the method of interfacial polymerization comprises the reaction of a dihydric phenol with diacid or derivative ester precursor and optionally a carbonate precursor, in a two phase system with catalyst and

often an acid acceptor when the dicarboxylic acid and carbonate precursors are diacid halides. Examples of interfacial polymerization techniques can be found in U.S. Patent Nos. 3,169,121 and 4,487,896 which are incorporated herein by reference.

5 Although the reaction conditions of the preparative processes may vary, several of the preferred processes typically involve dissolving or dispersing dihydric phenol reactants in aqueous caustic, combining the resulting mixture with a suitable water immiscible solvent medium and contacting the reactants with the carbonate precursor, such as, for
10 example, phosgene, and diacids or derivatives, such as diacid chlorides, in the presence of a suitable catalyst and under controlled pH conditions. The most commonly used water immiscible solvents include methylene chloride, 1,2-dichloroethane, chlorobenzene, toluene, and the like.

15 Advantageously a catalyst may be added to the reaction mixture to promote the reaction. The catalyst typically accelerates the rate of polymerization of the dihydric phenol reactants with the carbonate/ester precursors. Representative catalysts include but are not limited to, for example, tertiary amines such as triethylamine, quaternary phosphonium compounds, quaternary ammonium compounds, and the like.

20 The carbonate precursors are typically a carbonyl halide, a diarylcarbonate, or a bishaloformate. The carbonyl halides include, for example, carbonyl bromide, carbonyl chloride, and mixtures thereof. The bishaloformates include the bishaloformates of dihydric phenols such as bischloroformates of 2,2-bis(4-hydroxy-3,5-dichlorophenyl)-propane,
25 hydroquinone, and the like, or bishaloformates of glycol, and the like.

While all of the above carbonate precursors are useful, carbonyl chloride, also known as phosgene, is preferred.

In general, any dicarboxylic acid conventionally used in the preparation of polyesters may be utilized in the preparation of poly(ester-carbonate) resins. However, the PEC used in the present invention are prepared with aromatic dicarboxylic acids, and in particular terephthalic acid, and mixtures thereof with isophthalic acid.

Rather than utilizing the dicarboxylic acid per se, it is possible, and sometimes even preferred, to employ various derivatives of the acid moiety. Illustrative of these reactive derivatives are the acid halides. The preferred acid halides are the acid dichlorides and the acid dibromides. Thus, for example instead of using terephthalic acid or mixtures thereof with isophthalic acid, it is possible to employ terephthaloyl dichloride, and mixtures thereof with isophthaloyl dichloride

In the conventional interfacial polymerization methods of preparing PEC, and polycarbonates, a molecular weight regulator (a chain stopper) is generally added to the reaction mixture prior to or during the polymerization reactions with carbonate and/or ester precursors. Useful molecular weight regulators include, for example, monohydric phenols such as phenol, chroman-I, para-t-butylphenol, p-cumylphenol and the like.

The proportions of reactants employed to prepare the PEC will vary in accordance with the proposed use of the blends of the invention containing this product resin. In general, the amount of the ester units may be from about 0 by weight to about 90% by weight, relative to the

carbonate units, preferably about 0% to about 30% by weight relative to the carbonate units.

In general, any dicarboxylic acid conventionally used in the preparation of polyesters may be utilized in the preparation of 5 poly(estercarbonate) resins. However, the PEC used in the present invention are prepared with aromatic dicarboxylic acids, and in particular terephthalic acid, and mixtures thereof with isophthalic acid wherein the weight ratio of terephthalic acid to isophthalic acid is in the range of from about 5:95 to about 95:5

10 The preferred PEC for use as the ingredient (b) in the blends of the present invention are those derived from reaction of bisphenol-A and phosgene with iso- and terephthaloyl chloride and having an intrinsic viscosity of about 0.5 to about 0.65 deciliters per gram (measured in methylene chloride at a temperature of 25°C).

15 The Ar radical in the above formula is most often p- or m-phenylene, a cycloaliphatic or a mixture thereof. This class of polyester includes the poly(alkylene terephthalates). Such polyesters are known in the art as illustrated by the following patents, which are incorporated herein by reference.

20 2,465,319 2,720,502 2,727,881 2,822,348

3,047,539 3,671,487 3,953,394 4,128,526

Examples of aromatic dicarboxylic acids represented by the dicarboxylated residue Ar' are isophthalic or terephthalic acid, 1,2-di(p-carboxyphenyl)ethane, 4,4'-dicarboxy diphenyl ether, 4,4' bisbenzoic acid 25 and mixtures thereof. Acids containing fused rings can also be present,

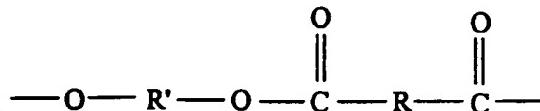
such as in 1,4-, 1,5- or 2,6-naphthalenedicarboxylic acids. The preferred dicarboxylic acids are terephthalic acid, isophthalic acid, naphthalene dicarboxylic acid, cyclohexane dicarboxylic acid or mixtures thereof.

It is also possible to employ two or more different dihydric phenols
5 or a copolymer of a dihydric phenol with a glycol or with a hydroxy- or acid-terminated polyester or with a dibasic acid or hydroxy acid in the event a carbonate copolymer or interpolymer rather than a homopolymer is desired for use in the preparation of the polycarbonate mixtures of the invention. Branched polycarbonates are also useful, such as are described
10 in U.S. Pat. No. 4,001,184. Polycarbonate blends include blends of linear polycarbonate and branched polycarbonate.

The preferred component c), the soft segment polycarbonate exhibit a lower glass transition (Tg) temperature and improved low temperature impact strengths. The Tg of the resin is reduced by the presence of diester
15 blocks.

U.S. patent 5,494,997 to Fontana et al describes the preparation of a thermoplastic, copolyestercarbonate by phosgenating the dihydric phenol in the presence or absence of an aliphatic dicarboxylic acid under conditions which yield an excess of chloroformate end-groups relative to
20 phenolic or carboxylic acid moieties; and polymerizing the chloroformates with remaining phenols and carbonate acids or with subsequently added aliphatic dicarboxylic acid by addition of a carbonate forming reagent and a molecular weight regulator. The above patent is incorporated by reference into the present application. The polyester resins of Formula I
25 as previously set forth are typically obtained through the condensation or ester interchange polymerization of the diol or diol equivalent component

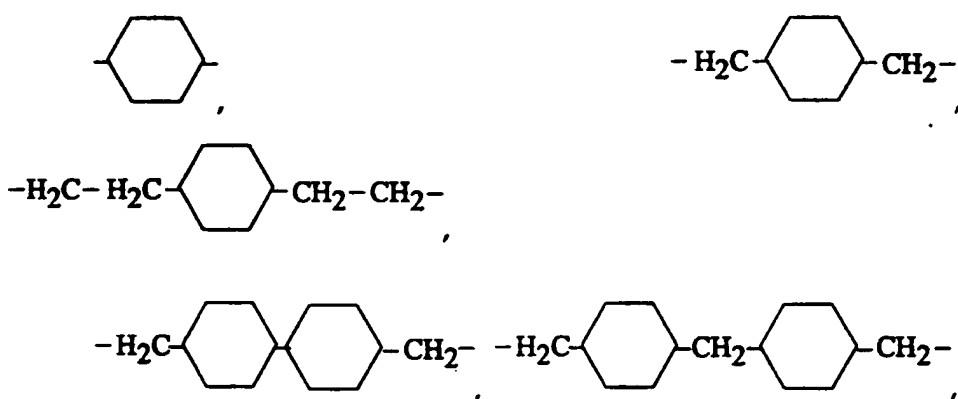
with the diacid or diacid chemical equivalent component and have recurring units of the formula where R is derived from alicyclic dibasic acids and R' is derived from a alicyclic diols R':

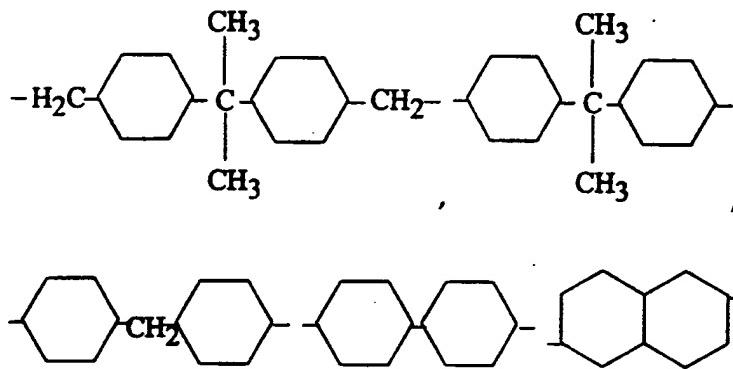


5 The preferred cycloaliphatic polyesters for use in the present molding compositions are condensation products of cycloaliphatic diols and cycloaliphatic diacids or chemical equivalents of the diacids such as the salts, esters or acid halides thereof. Preferably R is a cycloalkyl radical containing 6 to 20 carbon atoms and which is the residue of a cycloaliphatic
10 alkane diol or chemical equivalent thereof; and R' is a cycloalkyl radical which is the decarboxylated residue derived from a cycloaliphatic diacid or chemical equivalent.

R and R' are preferably cycloalkyl radicals independently selected from the following formula:

15





The most preferred cycloaliphatic radical R' is derived from the 1,4-cyclohexyl diacids and most preferably greater than 70 mole % thereof in
 5 the form of the trans isomer. The most preferred cycloaliphatic radical R is derived from the 1,4-cyclohexyl primary diols such as 1,4-cyclohexyl dimethanol, most preferably more than 70 mole % thereof in the form of the trans isomer.

Preferably a cycloaliphatic diol or chemical equivalent thereof and
 10 particularly 1,4-cyclohexane dimethanol or its chemical equivalents are used as the diol component, preferably a mixture of cis- to trans-isomers thereof, where the trans isomer content is 70% or more.

Chemical equivalents to the diols include esters, such as dialkylesters, diaryl esters and the like.

15 The diacids useful in the preparation of the aliphatic polyester resins of the present invention preferably are cycloaliphatic diacids. This is meant to include carboxylic acids having two carboxyl groups each of which is attached to a saturated carbon. Preferred diacids are cyclo or bicyclo aliphatic acids, for example, decahydro naphthalene dicarboxylic acids, norbornene dicarboxylic acids, bicyclo octane dicarboxylic acids,
 20

1,4-cyclohexanedicarboxylic acid or chemical equivalents, and most preferred is trans-1,4-cyclohexanedicarboxylic acid or chemical equivalent.

Cyclohexanedicarboxylic acids and their chemical equivalents can be prepared, for example, by the hydrogenation of cycloaromatic diacids and corresponding derivatives such as isophthalic acid, terephthalic acid or naphthaleric acid in a suitable solvent, water or acetic acid at room temperature and at atmospheric pressure using suitable catalysts such as rhodium supported on a suitable carrier of carbon or alumina. See, Friefelder et al, Journal of Organic Chemistry, 31, 3438 (1966); U.S. Pat. Nos. 2,675,390 and 4,754,064. They may also be prepared by the use of an inert liquid medium in which a phthalic acid is at least partially soluble under reaction conditions and a catalyst of palladium or ruthenium in carbon or silica. See, U.S. Pat. Nos. 2,888,484 and 3,444,237.

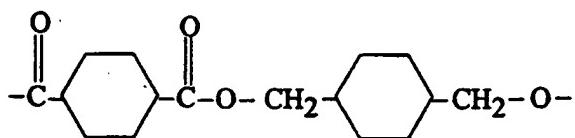
Typically, in the hydrogenation, two isomers are obtained in which the carboxylic acid groups are in cis- or trans-positions. The cis- and trans-isomers can be separated by crystallization with or without a solvent, for example, n-heptane, or by distillation. The cis-isomer tends to blend better; however, the trans-isomer has higher melting and crystallization temperatures and is especially preferred. Mixtures of the cis- and trans-isomers are useful herein as well, and preferably when such a mixture is used, the trans-isomer will comprise at least about 70 parts by weight.

When the mixture of isomers or more than one diacid is used, a copolyester or a mixture of two polyesters may be used as the present cycloaliphatic polyester resin.

Chemical equivalents of these diacids include esters, alkyl esters, e.g., dialkyl esters, diaryl esters, anhydrides, salts, acid chlorides, acid

bromides, and the like. The preferred chemical equivalents comprise the dialkyl esters of the cycloaliphatic diacids, and the most preferred chemical equivalent comprises the dimethyl ester of the acid, particularly dimethyl-trans-1,4-cyclohexane-dicarboxylate.

5 A preferred cycloaliphatic polyester is poly(cyclohexane-1,4-dimethylene cyclohexane-1,4-dicarboxylate) also referred to as poly(1,4-cyclohexane-dimethanol-1,4-dicarboxylate) (PCCD) which has recurring units of the formula:



10 With reference to the previously set forth general formula, for PCCD R' is derived from 1,4 cyclohexane dimethanol; and R is a cyclohexane ring derived from cyclohexanedicarboxylate or a chemical equivalent thereof. The preferred PCCD has a cis/trans formula.

15 The reaction is generally run in the presence of a suitable catalyst such as a tetrakis (2-ethyl hexyl) titanate, in a suitable amount, typically about 100 to 400 ppm of titanium based upon the final product.

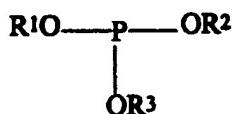
The preferred aliphatic polyesters used in the present reinforced molding compositions have a glass transition temperature (T_g) which is above 50°C, most preferably above about 80°C.

20 In the thermoplastic compositions which contain a polyester resin and a polycarbonate resin, it is preferable to use a stabilizer or quencher material. Catalyst quenchers are agents which inhibit activity of any catalysts which may be present in the resins. Catalyst quenchers are

described in detail in U.S. Patent 5,441,997. It is desirable to select the correct quencher to avoid color formation and loss of clarity to the polyester polycarbonate blend.

A preferred class of stabilizers including quenchers are those which provide a transparent and colorless product. Typically, such stabilizers are used at a level of 0.001-10 weight percent and preferably at a level of from 0.005-2 weight percent. The preferred stabilizers include an effective amount of an acidic phosphate salt; an acid, alkyl, aryl or mixed phosphite having at least one acidic hydrogen; a Group IB or Group IIB metal phosphate salt; a phosphorus oxo acid, a metal acid pyrophosphate or a mixture thereof. The suitability of a particular compound for use as a stabilizer and the determination of how much is to be used as a stabilizer may be readily determined by preparing a mixture of the polyester resin component and the polycarbonate and determining the effect on melt viscosity, gas generation or color stability or the formation of interpolymer. The acidic phosphate salts include sodium dihydrogen phosphate, mono zinc phosphate, potassium hydrogen phosphate, calcium dihydrogen phosphate and the like. The phosphites may be of the formula:

20



where R₁, R₂ and R₃ are independently selected from the group consisting of hydrogen, alkyl and aryl with the proviso that at least one of R₁, R₂ and R₃ is hydrogen.

The phosphate salts of a Group IB or Group IIB metal include zinc phosphate, copper phosphate and the like. The phosphorus oxo acids include phosphorous acid, phosphoric acid, polyphosphoric acid or hypophosphorous acid.

- 5 The polyacid pyrophosphates may be of the formula:



wherein M is a metal, x is a number ranging from 1 to 12 and y is a number ranging 1 to 12, n is a number from 2 to 10, z is a number from 1 to 5 and the sum of (xz) + y is equal to n + 2. The preferred M is an
10 alkaline or alkaline earth metal.

The most preferred quenchers are oxo acids of phosphorous or acidic organo phosphorus compounds. Inorganic acidic phosphorus compounds may also be used as quenchers, however they may result in haze or loss of clarity. Most preferred quenchers are phosphoric or
15 phosphorous acid.

Cycloaliphatic polyester resins have been found to have better weatherability than polycarbonate alone. Ultraviolet light absorbers are used to improve the polycarbonate light stability. Inclusion of a light stabilizer in a cycloaliphatic polyester/polycarbonate blend provides
20 additional light stability for the polycarbonate resin.

The ultraviolet light absorbers (UVA) useful in the present invention are those which are generally compatible with polycarbonates. Preferred are benzotriazole, benzophenone, triazine, cyanoacrylate, dibenzoylresorcinol, and oxanilide based UVA. Incorporation of a light
25 stabilizing additive in the PCCD composition, i.e., cycloaliphatic

polyester alone or a polycarbonate - cycloaliphatic polyester blend, provides additional benefits in weatherability.

In addition to UV absorbers, hindered amine light stabilizers (HALS) also contribute to increased weatherability of the structure.

- 5 Illustrative ultraviolet radiation absorbing compounds include 2-(benzotriazol-2-yl)-4-(1,1,3,3-tetramethylbutyl)phenol,
2-(benzotriazol-2-yl)-4-methylphenol, -hydroxy-4-octyloxy benzophenone,
2-hydroxy-4-methoxybenzophenone, ethyl-2,2-diphenyl-1-cyanoacrylate,
2'-ethylhexyl - 2, 2-diphenyl-1-cyanoacrylate, 2-(2'-hydroxy-4'-octyloxy)
10 bis-4,6-(2',4'-dimethylphenyl) triazine, 2-ethyl- 2'- ethoxy oxalanide, bis [2 -
hydroxy-5-methyl-3- (benzotriazol-2-yl) phenyl] - methane, bis[2 -
hydroxy- 5 -t - octyl -3 - (benzotriazol -2 -yl) phenyl] methane, 2,2' - (1,4 -
phenylene) bis [4 H - 3, 1 - benzoxazin -4 - one], and 2 - (2' - hydroxy-4 -
hexyloxy) - 4,6 - diphenyltriazine. Light stabilizers are incorporated in the
15 cycloaliphatic polyester e.g., PCCD, resin in amounts of about 0.05 to
about 10 weight percent.

- The ratio of polyester resin to ductile resin is from about 60 to 40 to
about 85 to about 15. Based on the total weight of ductile resin and
polyester resin, the composition preferably comprises from about 50 to
20 about 90 weight percent polyester, more preferably from about 65 to about
85 percent polyester, and more preferably from about 70 to about 85
percent polyester.

- It is contemplated that polycarbonate/cycloaliphatic polyester
compositions can contain up to 30% by weight of additional polymeric
25 binder materials in the blend, preferably less than 20 percent, and more

preferably less than 15 percent. Such additional ingredients may include polyalkylene phthalates or naphthanoates, polybutylene terephthalate polymers (PBT), polyethylene terephthalate polymers (PET), polypropylene terephthalate polymers (PPT), polyethylene naphthanoate polymers (PEN), polycyclohexane dimethanol terephthalates and styrene-acrylonitrile copolymers, preferably containing 25% - 35% of acrylonitrile. Additional, impact modifiers generally comprise an acrylic or methacrylic grafted polymer of a conjugated diene or an acrylate elastomer, alone, or copolymerized with a vinyl aromatic compound. In general these impact modifiers contain units derived from butadiene or isoprene, alone or in combination with a vinyl aromatic compound, or butyl acrylate, alone or in combination with a vinyl aromatic compound. Other typical impact modifiers include, but are not limited to ethylene vinyl acetate, ethylene ethylacrylate copolymers, SEBS (styrene-ethylene-butylene styrene) and SBS (styrene-butadiene-styrene) block copolymers, EPDM (ethylene propylene diene monomer) and EPR (ethylene propylene rubber) copolymers, etc.

The method of blending the present compositions can be carried out by conventional techniques. One convenient method comprises melt blending the polyester, acrylic, impact modifier and other ingredients in powder or granular form, extruding the blend and comminuting into pellets or other suitable shapes. The ingredients are combined in any usual manner, e.g., by dry mixing followed by mixing in the melted state in an extruder.

Additionally, additives such as mold releases, antioxidants lubricants, nucleating agents such as talc and the like, other stabilizers including but not limited to UV stabilizers, such as benzotriazole,

supplemental reinforcing fillers, and the like, flame retardants, pigments or combinations thereof may be added to the compositions of the present invention.

As set forth in the following examples, the properties are measured
5 according to the following procedures:

Notched Izod (NI) and Unnotched Izod (UNI): This test procedure is based on the ASTM D256 method. In this case, using Izod Method E, the unnotched impact strength is obtained by testing an unnotched specimen. The results of the test is reported in terms of energy absorbed
10 per unit of specimen width, and expressed in foot times pounds per inch (Ft.Lbs./In.). Typically the final test result is calculated as the average of test results of five test bars.

Dynatup® (DYN TE): This test procedure is based on the ASTM D3763 method and was performed on a Dynatup brand impact test
15 machine. This procedure provides information on how a material behaves under multiaxial deformation conditions. The deformation applied is a high speed puncture. An example of a supplier of this type of testing equipment is Dynatup. Reported as test results are the so-called total energy values at various temperatures, which are expressed in foot times
20 pounds (Ft.Lbs.). The final test result is calculated as the average of the test results of typically ten test plaques.

Melt viscosity (MV): This test procedure is based on the ASTM D1238 method. The equipment used is an extrusion plastometer equipped with an automatic timer. A typical example of this equipment would be
25 the Tinius Olson MP 987. Before testing, the samples are dried for one hour at 150°C. The testing conditions are a melt temperature of 250°C, a

total load of 5,000 gram, an orifice diameter of 0.0825 inch, and a dwell time of 5 minutes. The test result is expressed in the unit Poise.

Flexural Modulus (FM): This test procedure for measuring stiffness is based on the ASTM D790 method. Typical test bars have the following 5 dimensions: 1/8 inch by 1/2 inch by 2-1/2 inch. The final test result is calculated as the average of test results of five test bars. The test involves a three point loading system utilizing center loading on a simply supported beam. Instron and Zwick are typical examples of manufacturers of instruments designed to perform this type of test. The flexural modulus is 10 the ratio, within the elastic limit, of stress corresponding strain and is expressed in pounds per square inch (psi).

Gloss Retention (J1960 Gloss) - The J 1960 test is a SAE automotive specification for accelerated weathering, with gloss values measured using ASTM D523.

15 Color Retention (J1960 Color) - This test measures color change (Δ E) of the weathered sample using a Cielab System.

EXAMPLES

The following examples are set forth herein to illustrate in more detail the preferred embodiments and to illustrate more clearly the 20 principle and practice of this invention to those skilled in the art. They are not construed to limit the claims in any manner whatsoever. All compositional data are in weight percent unless otherwise indicated. Mechanical data represented is based on test methods according to Table 1.

Table 1

Mechanical Testing		
Abbreviate	Description	ASTM Test
MV	Melt viscosity at 250 °C in poise	D1238
NI	Notched Izod Impact Strength in ft. lbs./in.	D256
UNI	Unnotched Izod Impact Strength in ft. lbs./in.	D256
DYN TE	Dynatup Total Energy in ft. lbs.	D3763
FM	Flexural Modulus in psi	D-790

Examples of the invention E1 to E 17 as well as the control formulations C 1 to C 9 were prepared by blending all ingredients in a bucket blender until a good homogeneity of the blend was achieved. All
5 blend formulations were extruded on a vacuum-vented 30 mm WP twin screw operated at 500 F (dye head zone = 480 F).

Each of the following tables represents a set of experiments formulated with different batches of PCCD. These batches are equally formulated but differ slightly due to random process variation inherent to
10 any production.

EXAMPLES 1-4

Table 2 and Figure 1 elucidate the influence of different PCCD-to-PC ratios on the notched Izod values at room temperature. It can be seen that the notched Izod ductility (NI) increases with increasing PCCD content until it reaches a maximum of 24 ft. lb./in. (E3) at roughly 75 %
15

PCCD content. With further increasing PCCD content, the notched Izod values decrease again towards the notched Izod value of straight PCCD resin of around 12 ft. lb./in. Figure 1 also demonstrates the synergistic character of this invention: with increasing PCCD content in PCCD/PC blends the flexural modulus decreases linearly whereas the notched Izod curve exhibits a maximum at around 80 % PCCD. This behavior can be predicted by any known theory and was also not described for similar polymers in the literature.

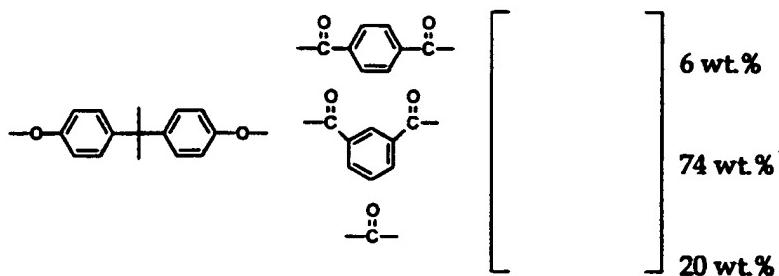
nb = no break

Table 2

EXAMPLES								
	C 1	C 2	C 3	E 1	E 2	E 3	E 4	C 4
Lexan Grade	100	100	80	65	50	35	20	10
PCCD Batch 1		20	35	50	65	80	90	100
Irgafos 168	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2
Irganox 1076	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2
Seénox 412S	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1
Phosphorus Acid	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1
MV [poise]	35000	22300	19000	16000	12300	9700	8600	6900
NI [ft.lbs./in.]	16	16	17	18	20	24	18	12
FM [psi]	13400	12800	11600	11000	9500	8400	7500	6900
FS [psi]	328000	308000	282000	259000	230000	207000	179000	165000

EXAMPLES 5-12

The general procedure of Example 1-3 is repeated with compositional adjustments. The formulations used and the results obtained are set forth in Table 3 which documents experiments with a fixed PCCD/PC ratio of 75/25 with dependence on different Lexan PC grades. All polycarbonate resins used are commercially available Lexan grades and differ mainly in molecular weight. Lexan SP is a soft-segmented Lexan 100 grade whereas the polyestercarbonate (PPC) is a BPA copolymer with isophthalic and terephthalic units described by the following structures displayed in



As can be seen, all examples (E 5 through E12) yield NI values of roughly 20 ft.lbs./in. and higher. It is remarkable that even a high flow version of Lexan 100 exhibit an impact resistance of more than 18 ft. lbs./in. as demonstrated in E5. Overall, it appears that fundamentally any BPA-based polycarbonate yields blends that are tremendously impact resistant. E 5 through E 12 also documents the robustness of the NI ductility achievable with high levels of PCCD.

Table 3

EXAMPLES

	E 5	E 6	E 7	E 8	E 9	E 10	E 11	E 12
high flow Lexan	24.8							
Lexan 100 grade		24.8						
Lexan 121 Grade			24.8					
Lexan 131 Grade				24.8				
Lexan 141 Grade					24.8			
Branched Lexan						24.8		
Polyestercarbonate							24.8	
Lexan SP								24.8
PCCD Batch 2	74.4	74.4	74.4	74.4	74.4	74.4	74.4	74.4
Irganox 1076	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2
Irgafos 168	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2
Tinuvin 234	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3
Phosphorus Acid	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1
MV [poise]	7220	9463	7909	11916	9123	14253	8183	14979
NI [ft.lbs./in.]	19	25	24	25	20	21	23	20
FM [psi]	212500	211500	212500	210000	208000	210900	205100	207300
FS [psi]	8343	8405	8324	8354	8476	8391	8030	8395

nb = no break

EXAMPLES 13-16

The general procedure of Example 4-12 is repeated making use of different core/shell as well as reactive copolymer impact modifiers. The ratio of PCCD/PC was kept identical to EXAMPLES 5-12 (75/25 ratio) 5 and the results obtained are set forth in Table 4. The impact modifiers used are Rohm and Haas EXL 3691, an MBS type modifier, Rohm and Haas EXL 3330, an Acrylic core shell modifier, and Elf Atochem Lotadar AX 8900 concentrate. Lotadar is a reactive EVA-Glycidyl Methacrylate copolymer dispersed in a polycarbonate matrix. Remarkably, the impact modifiers 10 used do not improve the ductility further, but decrease the stiffness (FM) of the blends with the exception of Lotadar AX 8900.

Table 4

EXAMPLES

	E 13	E 14	E 15	E 16
PCCD Batch 3	74.3	66.7	66.7	66.7
Lexan 100 Grade	24.8	22.2	22.2	22.2
R&H EXL 3691		10		
Lotadar AX8900 conc			10	
R&H EXL3330				10
MZP	0.1	0.1	0.1	0.1
Irgafos 168	0.2	0.2	0.2	0.2
Irganox 1076	0.2	0.2	0.2	0.2
Timuvin 234	0.4	0.4	0.4	0.4
MV [poise]	7200	11000	10100	10800
NI [ft.lbs./in.]	24.5	18	21.5	18
FM [psi]	165500	147500	163000	138000
FS [psi]	8700	7400	8500	7000

EXAMPLE 17

The general procedure of Example 13-16 is repeated making use of different polyesters as blend components. The formulations used and the results obtained are set forth in Table 5. The polyesters used are PBCD, poly(1,4-butylene cyclohexane dicarboxylate), PCT, poly(cyclohexylene dimethylene terephthalate), PBT, PET and Hytrel 4056. DuPont Hytrel 4056 contains roughly 50 % of a polytetrahydrofuran soft-segment in a PBT backbone. It can clearly be demonstrated that only PCCD/PC (E 17)

blends (75/25 ratio) obtain notched Izod values of more than 18 ft. lbs./in. All other polyesters (C5 through C8) exhibit notched Izod values that are significantly lower than E 17. It is also interesting to mention that only E 17, C 5 and C 6 are miscible and transparent blends whereas C 7 through C 5 9 are opaque.

Table 5

	EXAMPLES					
	E 17	C 5	C 6	C 7	C 8	C 9
Lexan 141 Grade	24.8	24.8	24.8	24.8	24.8	24.8
PCCD Batch 4		74.4				
PBCD			74.4			
PCT				74.4		
PBT					74.4	
PET						74.4
Hytrel 4056						74.4
Irganox 1076	0.2	0.2	0.2	0.2	0.2	0.2
Irgafos 168	0.2	0.2	0.2	0.2	0.2	0.2
Tinuvin 234	0.3	0.3	0.3	0.3	0.3	0.3
Phosphorus Acid	0.15	0.15	0.15	0.15	0.15	0.15
MV [poise] (test temperatures)	8710 (250)	3048 (250)	no flow (260)	6943 (260)	1440 (260)	3879 (250)
NI [ft.lbs./in.]	19	0.5	12	1.1	0.4	9
UNI [ft.lbs./in.]	31	29	37	38	41	12
Dyn TE [ft.lbs.]	41	34	42	36	24	25
FM [psi]	202500	250500	271000	344300	346900	65980
FS [psi]	8750	5010	11190	12790	12600	9380

Table 6 allegorizes the transmittance of a typical PCCD/PC blend (E 17) as a function of the light wavelength. As can be seen the blend maintains a transmittance of 80 % or more over the full range of visible light.

Table 6

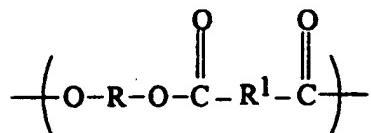
Wavelength [nm]	Transmittance [%]
400	79.3
420	88
440	88.5
460	88.8
480	89.1
500	89.3
520	89.5
540	89.7
560	89.8
580	89.9
600	90
620	90.2
640	90.1
660	90.1
680	90.2
700	90.2

Although the above examples have shown various modifications of the present invention, other variations are possible in light of the above teachings. It is, therefore, to be understood that changes may be made in the particular embodiments of the invention described which are within 5 the full intended scope of the invention as defined by the appended claims.

CLAIMS

What is claimed is:

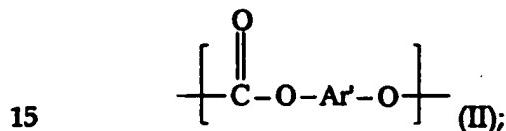
1. A ductile thermoplastic resin comprising a miscible resin blend of a ductile resin containing greater than about 50 percent by weight repeating units of an aryl polycarbonate, and a polyester resin wherein ratio of polyester resin to ductile resin is from about 50 to 50 to about 95 to about 5, said polyester resin consist essentially of a polyester having the formula I:



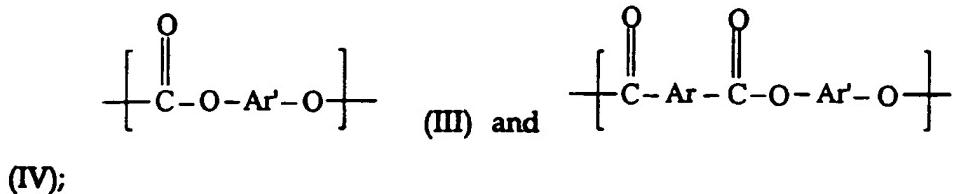
10 where R and R¹ are cycloakyl or cycloalkyl containing radicals.

2. A thermoplastic resin according to claim 1 wherein said ductile resin comprises a resin selected from the group consisting of

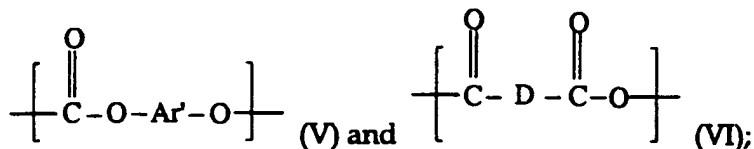
- a) a polycarbonate resin made up of recurring aryl polycarbonate units of the formula II;



- b) an aromatic polyester carbonate made up of recurring polycarbonate units of formula III and recurring aromatic polyester units of the formula IV;



- c) an aliphatic polyester carbonate made up of recurring polycarbonate units of the formula V and recurring aliphatic carboxylic ester units of the formula VI;
- 5



or d) mixtures of a) or b) or c),

wherein

- Ar' is a divalent aromatic radical residue of the dihydric phenol
10 employed in the preparative polymerization reaction of the polycarbonate;

Ar is a divalent aromatic radical, or mixtures thereof of the condensation product from a dicarboxylic acid or derivative thereof; and

D is the divalent aliphatic residue from the dicarboxylic acid

3. A thermoplastic resin blend according to claim 1 having an
15 effective amount of an alkyl, aryl or mixed phosphite having at least one acidic hydrogen; a Group IB or Group IIB metal phosphate salt; a phosphorus oxo acid, a metal acid pyrophosphate, said resin blend having an optical transmission of greater than 75 percent.

4. A thermoplastic resin blend according to claim 1 according to claim 2 consisting essentially of a blend of polycarbonate and cycloaliphatic polyester derived from a cycloaliphatic diol and a cycloaliphatic diacid.
5. A thermoplastic resin blend according to claim 1 wherein the polyester is cycloaliphatic polyester is poly(1,4 - cyclohexane dimethanol - 1,4 - cyclohexanedicarboxylate).
6. A thermoplastic resin blend according to claim 1 wherein R is the residue of a cycloalkane containing diol having 6 to 20 carbon atoms or 10 chemical equivalent thereof, and R¹ is the decarboxylated residue derived from a cycloalkane containing diacid of 6 to 20 carbon atoms or chemical equivalent thereof.
7. A thermoplastic resin according to claim 1 wherein the resulting blend has a Notched Izod (NI) as determined by ASTM D256 test 15 procedure greater than either the Notched Izod of the individual polycarbonate component or polyester component of the blend.
8. A thermoplastic resin composition according to claim 1 in which the resin blend of polycarbonate and polyester has a glass transition temperature above about 60°C.
- 20 9. A thermoplastic resin composition according to claim 8 in wherein Ar' is derived from a bisphenol-A, Ar is a terephthalic acid residue, D is a saturated aliphatic diacid residue of 8-16 carbons.
10. A thermoplastic resin composition according to claim 8 in wherin Ar' is derived from a bisphenol-A, Ar is a terephthalic acid residue, 25 D is a saturated aliphatic diacid residue of 8-16 carbons.

FIG. 1